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Geothermal Effluent Sampling Workshop

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16. ABSTRACT

This report outlines the major recommendations resulting from a workshop to identify gaps in existing geothermal effluent sampling methodologies, define needed research to fill those gaps, and recommend strategies to lead to a standardized sampling methodology.

The workshop, conducted by the Denver Research Institute at the University of Denver under U.S. Environmental Protection Agency sponsorship in May 1980, followed the Development Training Forum format. Invited participants from both public and private sectors contributed in establishing and preparing the recommendations, which covered gas sampling, two-phase gas sampling, liquid sampling, and quality control/quality assurance.

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GEOTHERMAL EFFLUENT SAMPLING WORKSHOP

by

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EXECUTIVE SUMMARY

Under U.S. Environmental Protection Agency sponsorship, the Denver Research Institute at the University of Denver hosted a workshop to:

- o Identify gaps in existing geothermal effluent sampling methodologies,
- o Define needed research to fill those gaps, and
- o Recommend strategies to lead to a standardized sampling methodology.

The workshop was conducted in early May 1980 and followed the Development Training Forum (DTF) format. Invited participants from both public and private sectors contributed ideas, discussions, and detailed writings in the sessions of Quality Assurance/Quality Control, Gas Sampling, Two-Phase Sampling, or Liquid Sampling. A plenary session was devoted to establishing the constraints and consisted of presentations on Release Points, Process Additives, and Pollutants of Concern.

The major recommendations resulting from the workshop were:

Gas Sampling	- Develop a continuous in-line monitor for noncondensibles. - Develop a continuous in-line monitor specifically for hydrogen sulfide (H_2S). - Develop instrumentation and methods for cooling tower emissions. - Develop sampling techniques to characterize fluids in a pipeline. - Develop and/or validate mercury sampling and preservation techniques in a reducing atmosphere. - Characterize the chemical composition of matrix gases (steam). - Develop a reliable field analyzer for H_2S. - Develop a sampling technique for noncondensibles, such as boron or arsenic, which partition into the liquid phase. - Determine the inertness of stainless steel for H_2S sampling applications.
Two-Phase Sampling	- Obtain best sample near the wellhead. - Install two sampling ports at 90° or in a porcupine configuration.

- Establish full capacity well flow to develop steady-state conditions.
- Sample isokinetically if flow rate in known.
- Develop a time-integrated method to deal with solids in multiphase flow.
- Develop a sample port seal to allow probe to traverse fluid stream.
- Design probe to collect representative fraction across flow stream.
- Design probe to obtain grab samples.
- Investigate probe material compatibility with fluid.
- Determine probe shape effects.
- Determine parameters of collection trains, e.g., filter, phase separator, impinger, pressure/temperature (P/T) requirements, pressure drop.
- Investigate flow measurement devices, pitot tubes, venturis, mass flow meters.
- Investigate fluid mechanics using probes.
- Determine chemical concerns in multiphase sampling.
- Describe physical and chemical parameters of multiphase flow.
- Evaluate sampling hardware.
- Match sampling technique(s) to application of results (i.e., research vs regulatory compliance).

Liquid Sampling

- Define categories of effluent as: supply, conversion, or release point.
- Define use of sample as: research/engineering, or regulatory.
- Recognize site specificity.
- Agree on sampling points.
- Agree on sampling port type and configuration.
- Agree on pressure/temperature sampling conditions.
- Maintain records, including P/T and flowrate.
- Develop reporting criteria.
- Demand unit standardization (S.I.).
- Specify preservation techniques.
- Establish sample history.
- No vacuum filtration if volatiles or pH changes expected.
- Develop in-line monitoring.
- Filter natural effluents through a 0.45-micrometer filter.
- For preservation, lower pH to 3 or less with high purity nitric acid.

- For total dissolved solids (TDS), preserve by dilution.
- Analyze mercury on site.
- Use glass containers with polyseal caps except for samples requiring silica analysis.
- Do not acidify turbid samples--recognize the potential of precipitation on adding acid.
- Maintain samples in a dark environment and ambient temperature, and transport promptly.
- Outline sampling procedures for byproducts holding ponds, direct release, closed loop, cold water injection (See Text).
- Determine the effects of dissolved ozygen.

Quality Assurance/ Quality Control

- Relate degree of hazard to need for accuracy.
- Provide for alternative sampling methods.
- Allow for a flexible system that is site specific.
- Provide a data base of sampling and analytical methods.
- Facilitate the cooperative development of methods.
- Utilize a matrix method of integrating site, pollutant, and release points.
- Evaluate the components of variance.
- Develop sampling techniques that will accurately monitor effluent discharge, are accurate, precise, and repeatable, and are readily and inexpensively implemented.

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INTRODUCTION

In an effort to assist the U.S. Environmental Protection Agency (EPA) identify gaps in geothermal effluent sampling methodologies; to define needed research to fill those gaps; and to recommend to EPA strategies to lead to standarized methods of sampling geothermal effluents, a workshop was held in Las Vegas, Nevada, hosted by the Denver Research Institute. The workshop was intentionally limited to a small number (30-35) of participants. To ensure the most comprehensive expertise, participants were selected from various sectors, representing differing degrees of involvement in geothermal sampling. Those attending included representatives from both the public and private sectors.

Based on the needs identified by EPA, the workshop methodology utilized was the Development Training Forum (DTF), in an effort to obtain the most optimal results. The purpose of DTF is to shape a comprehensive practical development model geared to the interest of the forum's participants. The techniques of DTF were designed to structure the group's "collective" wisdom; the content of each session comes from the participants, not the methodology. In contrast to approaches which begin by establishing ideals or superimposing goals, the methods are fundamentally indicative. The internal structure of each workshop is composed of three methodological steps--brainstorming, gestalting, and consensus.

In brainstorming, the workshop leader attempts to elicit as much data as possible. All data are accepted and written down as each person, in turn, contributes one idea at a time. Once the group is satisfied with the areas identified, gestalting begins. Gestalting is the process of grouping all the data from the brainstorm step into similar categories. The group then assigns a name to each major category. Naming the categories is the way the group can assimilate large amounts of diverse data and continue to make decisions about it. This process rationally orders the intuitions of the whole group. The result of this product is the consensus itself. Because the wisdom of the whole group rather than just the outspoken few is considered, this step allows the work produced to become a consensus of the group, adopted and accepted by all. Each participant then assigns a value to the major categories on a scale of 1-10. All of the numbers are added for each category, and the total number is divided to obtain respective rankings. The entire group has participated in the design of the model and, therefore, everyone supports the product.

In order to ensure that all participants started from a common knowledge base, three plenary sessions were conducted. The first, "Release Points," identified actual and potential points of effluent release from a surface system. The second session, "Process Additives," considered the effects of scale control additives, etc. The third session, "Pollutants of Concern," defined those pollutants of particular importance to EPA.

Each participant identified the workshop of his or her choice. The workshops were: 1) Quality Control/Quality Assurance, 2) Two-Phase Sampling, 3) Liquid Sampling, and 4) Gas Sampling. The final results of each group are detailed in the following section.

QUALITY ASSURANCE/QUALITY CONTROL

The QA/QC Workshop participants identified the following major points of concern:

- o Accuracy/Precision in Sampling
- o Validity of Sampling Logic
- o Development and Use of Models
- o Comparibility of Results
- o General Policy Perspectives

ACCURACY AND PRECISION IN SAMPLING

Introduction

Following the recommendations of this workshop, guidelines and recommendations for geothermal effluent sampling will be developed to ensure the collection of representative ("best") samples within the limits of technology and the requirements of the intended specified use. Essential to the quality control of the final resultant analyses are the determination and specification of the precision (repeatability) and accuracy (truth) of the sampling and analytical procedure. We here assume the integrity of the analytical procedure and consider sampling to include the collection, as well as all physical and chemical treatment of samples, between their source and chemical analysis. As this will generally involve a number of sequential operations, errors introduced at any step will be perpetuated throughout the procedure.

Discussion

Geothermal systems and natural geothermal materials are neither homogeneous nor static. Sampling methods are never strictly repeatable. Analyses of geothermal samples are thus always, at best, random estimates of the chemistry of the larger body of geothermal material of interest. Estimates of the precision and accuracy of the analyses are as important as are the absolute values. We recognize an important gap in our understanding of the components of variance within geothermal sampling methodologies including:

- o various sampling methods
- o sample preservation and handling procedures (chemical: additives, vessel composition; physical: temperature, pressure, containment, time between collection and analysis)
- o sensitivity to operator differences
- o chemical analytical procedures (not addressed here)

We recognize an important need for research directed toward the definition of variance within sampling equipment and procedures.

Analytical values reported are of limited value unless the specifics of all procedures along with estimates of the quality of the data are also reported. This documentation of sample history is essential for critical evaluation of the data and permits repetition of the operation if necessary. We recognize the need to include documentation regarding sample treatment within required effluent sampling and analysis reports. Technically, it is probably possible to develop sampling and analytical hardware and procedures which can meet any desired level of precision and accuracy. At some point, this becomes neither necessary nor desireable if it proves to be a prohibitive burden upon the resources of the operator or regulator. We thus recognize the need to define the limits of accuracy and precision which need to be met for reporting effluents. It seems reasonable and desirable that these would vary depending upon the potential environmental danger of the constituent, the levels of the species present, and expected magnitude of natural variation. For example, it might be acceptable to know the concentration of some relatively benign elements present at levels well below established standards to an accuracy of $\pm$ 50% or $\pm$ 100%, whereas for other potentially more hazardous elements present at near-standard levels, accuracies of $\pm$ 5% might be required to assure proper protective monitoring. Similarly, the frequency of sampling necessary for effective monitoring in these two instances could well be different depending upon observed system transience. Establishment of quality control specifications is necessary before standardized procedures can be established.

Despite the best hardware and methodologies, sample quality control must always consider operator-induced variation and error. Establishment of an effective sampling program must include the preparation of appropriate documentation and perhaps the institution of training programs to ensure that persons responsible for the collection of samples are properly trained and equipped to accomplish their task.

VALIDITY OF SAMPLING LOGIC

QA/QC methods may vary as a function of site characteristics. There must be an ability to prescribe various specific sampling methods and frequencies that will:

- obtain representative samples and establish flow rates within ranges of produced fluid variables of phase, temperature, pressure, flow, and chemical character;
- accommodate differing types and rates of waste disposal; e.g., cooling towers, waste fluid injection, waste fluid surface drainage discharge, gas ejectors, storage ponds (solids and brines);
- be appropriate to the character of waste fluids vs land use, water use, and/or character of the biological system in the vicinity: e.g., arid desert may be low risk--thus, less precision and accuracy will suffice; or, as another example, agriculture use may require measurements of different constituents than those of drinking water.

Sampling QA/QC criteria should be established, perhaps subcategorized as to site characteristics.

The validity/applicability of a sampling logic in meeting a specific purpose is often demonstrated by an iterative process (an example is repetitive sampling using various techniques and equipment). This process continues until consistency (or acceptable inconsistency) is found in arriving at reasonable answers as to effluent quantities. (Another example is that of "practice makes perfect," or one sampling method being used repeatedly until it is used with consistent adeptness.)

Effort should be expanded toward reducing the magnitude of the iterative process while maintaining confidence in the validity.

QA/QC emphasis may differ depending upon project maturity (i.e., development phase vs operational phase). In the initial exploratory phase, order-of-magnitude results may suffice as a prelude to a decision on whether to proceed. In power plant design requirements, results of high precision and accuracy may be demanded where, for example, scaling or corrosion problems are indicated.

Emphasis in the development phases may be upon wellhead or in-line sampling to predict process events and effluents; methodologies may be reasonably comparable but not standardized. In the operational phase, the emphasis may be upon end-of-pipe effluent sampling with preferably standardized methodologies.

QA/QC criteria should be developed for each development phase (after phases are defined) based upon the purposes of sampling.

DEVELOPMENT AND USE OF MODELS

Introduction

Data obtained from sampling in the field have their greatest utility in the context of a model about processes and pathways. Such models can be mathematical constructions of a flow stream within a power plant or of the dispersion and decomposition of an effluent material in the environment after it leaves the geothermal development site. The detail used in constructing these models reflects understanding of the processes and pathways involved and also the significance of the specific effluent to environmental concerns. Some models involve the concept of compartments of the plant or environment within which the effluent material has a concentration, a residence time, and a propensity to become involved with chemical productions. Additionally, there are concepts of transport between compartments. Often the transport is less than complete, indicating that the effluent material is either accumulating upstream or being chemically changed.

The results of sampling provide the numerical data with which to calibrate compartments within a model that relates to an operation and its environmental impact.

This concept of model emphasizes the dynamic nature of pollutants, their sources and their sinks. Additionally, it emphasizes that a foundation obtained about the effluent material in one compartment can be used to infer something about that same material in another compartment downstream or upstream--if something is known in a general way about the transfer processes. The more knowledge available about the transfers and residence time, the less data are required for the concentrations of materials in the successive compartments, in order to yield a satisfactorily accurate model.

In evaluating an environmental impact, data about some compartments are more useful than data about other compartments. The construction of the model gives guidance about which compartments are most cost-effective to sample. Thus, a model provides the logical basis for sampling; the samples provide a numerical calibration for the model.

As a practical matter, models are not made so complicated that they are perfect imitations of the real environment and impacts upon it. Perfect models cannot exist because all the transfer coefficients and other fundamental aspects cannot be obtained with perfect precision or in perfect concert with factors of timing.

Useful models are those which deal with the compartments and transfers involved with the social interests of environmental impact and to which engineered modifications can be applied. It is important to emphasize that engineering solutions to environmental impacts are seldom practical to apply to the environmental compartment in which the impact occurs. Rather, they are applied at some place upstream in the pathway. Thus, two generic kinds of models will be useful in geothermal regulations: one deals with the environmental issues, the other with the plant operations. Furthermore, the models for plant operations can be divided into those for plants actually operating and for those for plants proposed to be built. The two kinds of models for plant behavior are the main items of concern in this section.

Models For Operating Plants

This category of model generally can be very concrete. The compartments to be sampled are available throughout the whole process stream. Questions about transfers between compartments can be resolved by sampling, usually in a straightforward way. Issues will tend to emphasize representativity of the sampling method and accuracy of analysis. Questions about the validity of the model itself, whether certain compartments, transfers or processes in the model have their counterpart in the real system will be scarce, perhaps involving third order effects. If environmental measurements show an operating plant to be out of compliance, the model will help focus on the reason so that mitigation efforts can be applied in the most cost-effective places.

Sampling done to calibrate models of operating plants in principle can yield a precision for each sampling point that is as high as desired. A full description of each release point involves concepts of average value for a concentration, the range of values that are measured (due jointly to random uncertainties in the sampling/analysis and to real variability in the effluent

concentration.) Additionally, few compartments contain a uniform concentration of components overtime, hence, some information about trends and cycling may be important.

In real plants some release points are not always active and some of those may not be sampled even when they are active. Such release points deserve to be part of the model. The justification for sampling them consistently, or not, can be based on their relative contribution to the overall effluent releases. The contribution may be measured by temporary programs set up specifically for the task, or perhaps estimated by knowledgeable individuals. The attention given to quantifying the input of a single release point could depend jointly on whether that point was a second or third order contributor to the total effluent and whether the estimated contribution was smaller than the uncertainty permitted in the assessment of total releases. Plant models should have a category for nonsampled releases and an estimate of their contribution.

Models For Proposed Plants

Before use permits can be issued, some evidence is required to assure that excessive releases of pollutants will not occur. Questions about this issue cannot be answered directly because the effluents in question do not then exist. Indirect answers are provided by mathematical models or by analogy with operating plants of similar design using a similar resource. When a new geothermal field is developed, a satisfyingly analogous operating plant is not likely to be available. All parties must then rely on some sort of mathematical modeling of the plant's (expected) behavior.

Data for these models come from sampling and analysis of the resource done during (probably) short periods using process streams different from those involved with the plant for which permits are desired. In these cases, the validity (appropriateness) of the model is a much more serious issue than is the sampling/analysis. In a pioneering development the applicant carries a great burden in designing a model which gives an accurate forecast. He works under a real threat of being disallowed to continue operations if the real effluents, measured after startup, are substantially more than predicted by the model.

This burden is all the greater in practice because several plant designs will likely be considered by the applicant before an optimum one is selected for permitting. Each will have a separately tailored effluent model, used in the preliminary evaluations made by the applicant for private purposes.

In these models, data from sampling/anaylsis are stretched the farthest in the sense that results about one compartment are translated to behavior in another, perhaps not even in the same process stream. The uncertainties are sometimes large and expectations for accurate predictions should be considered in that context. Retrofit of engineered methods that were seriously underestimated for reducing effluent might be considered if the impact from that effluent would be troublesome.

Importantly, this is the place where models about environmental pathways and impact should be brought into focus. The environmental models of the environs about the plant site are similarly uncalibrated and speculative. These models deserve to be recalibrated with new data at the same time a new plant starts up. It should be clearly verified whether the environmental model overestimates an impact due to the effluent in question.

Summary

Three kinds of models are fed with data from sampling/analysis of the geothermal resource: proposed plants, operating plants, and environmental impact. Each kind of model involves distinct uses of the data and a unique arrangement and degree of uncertainties. The requirements for data are dissimilar; the focus of each model identifies the kind and quality of data which are best used in calibration. It can scarcely be over-emphasized that the model is only a fact of reality not the real thing, even though field data are used. Most of the important conclusions about the plant's function and the environmental impact will concern numerical operations using the data. This is especially true for proposed plants and for the nearby areas they are expected to affect.

Effluent materials within individual compartments of the models and the realities they represent are characterized by an average concentration, an uncertainty/variability for any instant, and by a trend or cycling over longer times. To the degree those factors are relevant to the environmental impact, they should be explicit parts of the model and of the sampling/ analysis program.

The models are necessarily inexact imitators of reality, so it is important to verify that simplifications be confined to second and third order factors. As a point of view, the model represents reality and the data calibrate the model.

COMPARABILITY OF RESULTS

The basic QA/QC goal is the establishment of comparability of results on three bases:

- o interorganizational comparison,
- o comparison between past and present,
- o intraorganizational comparison.

The results will be comparable in all three of these bases if the data are both reproducible and traceable as to the methodologies and equipment that was used.

There are several difficulties that must be kept in mind when designing a QA/QC system to specifically address the comparability of results. Certain sites or wells are sufficiently different from others so that methodologies have been (or will be) modified to suit the particular site. The QA/QC system must be flexible enough to recognize this. There will be a problem in time degradation of some fluid characteristics between time of extraction and the

time of analysis. Sampling hardware differences can affect the sample that is extracted both from contamination and preferential bias standpoints.

In designing a QA/QC system for these systems, three things should be emphasized.

- The QA system must encourage the simplest methodology to do the job. This minimizes both the possibility of error and the training/labor/capital costs.
- The need for accuracy/precision may vary because of differing needs:
  a. between organizations
  b. with time
- Any change in methodology should be documented so results taken at two different times can be related even if different techniques were used.

Within this framework there are two generic types of QA/QC systems that can be used to provide comparability of results. These are:

- Institutionalizing methods via regulation or a standardizing organization
- Cooperative comparisons via participation in exercises designed to evaluate only the suitability of the generated data.

The institutionalized method option, if it addressed all the factors that influence reproducibility and traceability, would concern itself with:

- personnel (training, certification)
- hardware
- sampling procedure
- sample preservation

This option provides a great deal of control, but a corresponding decrease in flexibility for the users.

The cooperative comparison option involves participation in multiorganizational exercises to compare the resulting data to established or mean values. This is widely used in the context of evaluating laboratories where there is proliferation and dynamic nature to overlapping methods. This option would:

- Evaluate only the end result leaving the organization free to choose the method.

- o Be difficult logistically and facility-wise to implement for sampling on an ongoing basis.

- o Provide a comparability statement based at a particular point in history to relate that to the future, each organization must have a QA plan to assure consistency and document any changes.

This option provides more flexibility to the user, but it provides a corresponding decrease in control.

Some regulatory bodies use a blend of the two options to certify performance--California in certifying analytical laboratories, for example. It might be that one or the other, or a blend of the two options, might be used to certify sampling specialists. Such individuals or organizations might then have the flexibility to tailor methods to new and unique situations with some assurance that the results would be comparable to what other specialists would report.

GENERAL POLICY PERSPECTIVES

This category received the lowest priority rating, but it was the concensus of the group that it is an important aspect for consideration since it recommends future policies. The low priority was probably the result of feelings that these were things that could not be immediately instituted by this group.

Differences between Engineering and Environmental Objectives

Engineering QA/QC objectives are to identify both continuous and possible effluent release points and appropriately monitor either these or upstream points in order to operate the system to meet environmental standards. Since an operating system is dynamic, quite often if not most often, this will involve upstream sampling and insertion of the data into a model to predict the effluent levels under present operating conditions.

During the design and permitting stages, the resource sampling QA/QC is most important and in the domain of EPA since plant design and predicted effluent levels depend on the accuracy of the sampling data and handling of that data in the model.

During operation, engineering QA/QC may be important in litigation of compliance disputes.

Environmental QA/QC objectives are to ascertain that system operation is at or below effluent compliance levels either "at end of pipe" or "at point of impact." Which point is most important may be site specific and QA/QC measures will differ accordingly. In either case both concentration and mass flow should be integrated to obtain total amount/time period.

Unanticipated Events

In the particular case of injection of fluids, there is little history on which standards can be based as well as uncertainties as to the possible appearance of effluents in the biosphere at some later date. Research in establishing base line data is suggested and understood to be proposed at the present time.

In the area of catastrophic failures, for whatever reasons, systems should be designed to minimize release of undersireable constituents, i.e., normally open/normally closed valves installed to shut off or direct flows, etc.

In cases where there are uncontrolled releases, the policy should be to evaluate the release in proper perspective. For example, a ruptured steam supply line at the Geysers may release considerable amounts of contaminants but the release may be relatively small in relation to the normal operation of the total system and not a justifiable cause to shut down the entire operation or even the power plant the line supplies.

Goals for Accuracy and Precision in Estimating Releases

Sampling accuracy and precision should realistically reflect the hazards and/or deleterious effects. Sampling and analysis cost usually rise drastically with increased accuracy and frequency and may not be justifiable. Where compliance levels are well below minimum hazard levels (and they usually are) accuracy and precision can be reduced. If sudden increases or increasing trends are detected, precision and accuracy should be increased to closely monitor the events or trends.

GAS SAMPLING

The Gas Sampling Workshop participants identified the following major points of concern:

- o Continuous In-Line Monitoring
- o Cooling Tower Effluent Methods and Instrumentation
- o Pipeline Sampling
- o Mercury Sampling and Fixing
- o Matrix Gases
- o Field Analysis for H_2S
- o Nonvolatile Sampling and Relation to Original Steam Composition
- o Sample Degradation

CONTINUOUS IN-LINE MONITORING

The only satisfactory method of determining the temporal variance of the noncondensible gases in a geothermal system is to continuously monitor the gas concentrations. Regulators are concerned with continuous monitoring to make sure that an emission source is in compliance with the applicable regulations. Power plant operators could use a continuous monitoring system to more efficiently control hydrogen sulfide (H_2S) abatement systems and steam producers could use the information as a tool to evaluate the reservoir. Presently there are no techniques or instrumentation available to monitor noncondensibles in a steam system on a continuous basis. Research needs to be undertaken to develop such a monitor.

An element of concern to all parties is H_2S. California has the most restrictive H_2S air quality standard to date and basically regulates this element under a nuisance criteria, though the data base for long term low level exposures to H_2S are generally lacking, which may establish concerns under public health criteria.

Basically, control of this element has been through chemical additives such as hydrogen peroxide. These costly components also require that uses be as minimal as possible but still sufficient to assure compliance with any specified emission limitation.

The emission limitations on H_2S play an additional role in that if total amounts are less than Federal revision requirements in this controlled state, the development of geothermal resource may proceed with only local governmental agency review.

Considering the dilemma of permitting resource developments and utilization with limited data and anticipated environmental impacts, if levels of H_2S are maintained at a specified level, the need to have a continuous monitor is of vital concern.

This monitor must be capable of sampling a wide range 10 parts H_2S per million [water] (ppm_w) → 1000 ppm_w H_2S in a very hostile environment.

RESEARCH AND DEVELOPMENT OF METHODS AND INSTRUMENTATION NEEDED TO DETERMINE COMPONENTS IN COOLING TOWER EMISSIONS.

Cooling tower emissions are a source of air pollution. The cooling tower releases gaseous products, vapors, liquid droplets, and particles. The major gas pollutant is H_2S. Hg and radon are of lesser concern. The major pollutant emitted in the liquid droplets (drift) is boron. Arsenic and possibly other metals in the droplets are of lesser concern. Chemicals added to control H_2S emissions may also be emitted from the cooling tower.

In order to understand the efflux from the cooling tower, dispersion of the pollutants into the atmosphere, and their eventual disposition, it is necessary to study the cooling tower emissions characteristics. Pacific Gas & Electric Company and Environmental Systems Corp. have performed some studies on specific cooling tower(s). Similar research is needed, and other parameters in addition to those measured in the above study should be investigated. Improvements in the measurement techniques (e.g., temperature) used in the above study should also be investigated.

RESEARCH NEED FOR SAMPLING TECHNIQUES TO CHARACTERIZE FLUID IN PIPELINE (P/L) CROSS-SECTION.

In order to obtain representative samples of gases in a P/L transporting steam to a power plant, an understanding of the fluid characteristics, which may vary spatially across a P/L, is needed. At the Geyser's for example, it is thought that water film forms along the walls of steam transport P/L and a homogeneous mixture of gases and water vapor flow through the central portion of the P/L. This assumption has been made due to the extreme turbulence of high velocity steam flow causing the gaseous phase to be well mixed (homogeneous). Thus present sampling techniques have been accomplished by drawing the sample from the center of the P/L. The validity of this technique should be checked by research into the spatial distribution of the liquid phase across the P/L section.

RESEARCH METHODS FOR SAMPLING AND FIXING MERCURY SAMPLES.

Currently, Union Oil collects mercury samples into a trap containing a dilute, acidified solution of $K_2C_2O_7$. This method should trap inorganic and elemental mercury, but probably not organic mercury which is not a serious problem since elemental mercury is considered to be the dominant form. The real problem is the H_2S in the steam which reduces the $Cr_2O_7^{2-}$ to Cr^{3+} leading to a potential loss of mercury. This cannot be overcome by adding a large excess of $K_2Cr_2O_7$ since this would interfere with the subsequent analysis (generation and vaporization of elemental mercury with atomic absorption analysis). Currently, sampling is terminated when the orange $Cr_2O_7^{2-}$ color is discharged and the green Cr^{3+} color is dominant; then an additional quantity of $K_2Cr_2O_7$ is added to preserve the sample. Is this procedure adequate to ensure good mercury samples or does a better method exist to sample mercury in this reducing medium?

RESEARCH LEADING TO A BETTER UNDERSTANDING OF MATRIX GASES - CHEMICAL STATE AND CHEMICAL INTERACTION OF COMPONENTS

The chemical state of constituents in the matrix gases (steam) is not well characterized. For example, is Hg present as Hg vapor and/or volatile Hg ++ compounds? Chemical component interactions (or influences) are important in some instances. For example, the ammonia concentration level influences the solubility of H_2S. Understanding (or realizing this influence) is important when considering an H_2S abatement process.

Research is needed to better characterize the chemical composition of geothermal steam in order to design good sampling methods and to provide information valuable for process design.

RESEARCH INTO RELIABLE, EFFECTIVE FIELD ANALYZER FOR THE DETERMINATION OF H_2S

Several effective methods are available for the determination of H_2S in steam. For example, (1) the iodmetric titration and (2) the silver nitrate titration. These are multiple-step, reagent-intensive methods that are performed by trained technicians.

There is a need to develop a field instrument, preferably battery-operated, that would be simple to operate, require no chemical reagents, be easy to standardize, be useful over a wide range of concentrations, and be acceptable to a wide diversity of users.

NONVOLATILE SAMPLING

The analysis of volatile components of high quality steam either at the wellhead or in the pipeline can be accomplished in a relatively straightforward manner which will be described below. However, the analysis of non-volatile components (e.g., Boron and Arsenic) is not straightforward since these components partition into the liquid phase which is inevitably present in even high quality steam. This amounts to a two-phase sampling problem, and it was suggested that the best strategem to solve this problem would be to sample the condenser water then calculate to a total steam basis.

At the wellhead, the sampling port is the bleedline which should be purged to heat the line before sampling. No probe is used. In the pipeline, the port should be placed in the top or side of a straight section and the probe should be inserted into the center of the line. The size and position of the probe are of no consequence unless isokinetic sampling is required, in which case the probe should face into the flow and the size should be selected to provide a reasonable sampling rate. There was some concern over whether stainless steel is a suitable probe material (Sample Degradation in Sampling Line) but the residence time is so low that this was generally considered not to be a problem.

The sampling train consists of a flexible transfer line with a valve to control the sampling rate and a condenser. The total flow from the condenser (condensate + non-condensibles) is passed through a gas dispersion tube into a scrubbing solution appropriate for the analyte of interest (H_2S, NH_3, CO_2,Hg),

then the non-condensibles flow through the reagent bottle into a suitable volume-measuring apparatus (e.g., wet test meter, graduate). Non-condensibles can be measured by eliminating the scrubbing reagent, weighing the condensate, and measuring the volume of non-condensibles. Hydrocarbon sample of the non-condensibles can be collected in glass sampling containers for subsequent gas chromatograph or mass spectrometer analysis.

SAMPLE DEGRADATION IN SAMPLING LINE.

The sampling probe and condenser in the sampling train are typically made of stainless steel. One should ask whether the particular gas being analyzed (e.g., H_2S) reacts with the stainless and, therefore, biases the samples. The experience at the Geysers over the last 15 to 20 years seems to indicate that corrosion of steel is not a major problem. Also, since the residence time in the probe and condenser is so short, one would intuitively conclude that reaction with the stainless is no problem. However, the inertness of stainless has not been demonstrated.

TWO-PHASE SAMPLING

The Two-Phase Sampling Workshop identified numerous topics of concern within each of the three major categories:

- o Identification of Existing Gaps
  - What is Required Information?
  - Sampling Strategy
  - Required Accuracies
  - Reproducibility of Results
  - Sample Preservation
  - Effects of Solids
- o Definition of Research Needs
  - Sampling Hardware
  - Fluid Mechanics
  - Chemical Concerns
  - Policy Guidelines
- o Strategies for Standardization
  - Physical/Chemical Description
  - Evaluation of Hardware
  - Use of Appropriate Techniques
  - Applications of Techniques

IDENTIFICATION OF EXISTING GAPS

"What is required information in two-phase sampling?"

This is a complicated situation, different groups have different questions.

- o A power plant designer will be concerned with steam quality, noncondensible gases, corrosion potential (pH, eH, metal ions) and scale constituents ($CaCO_3$, SiO_2).
- o Someone interested in mineral recovery or someone interested in pollutants may be concerned with trace metals and noncondensibles.
- o A field operator may be concerned with many of the same subjects as the power plant designer, but with different emphasis (life of the resource, injectability).

For some uses total flow measurements are adequate (where practical); for other uses, detailed answers about the pipe and its regimes may be required.

In general, there are two questions to be asked:

- o What information do we need?,
- o How do we get it?

First: We generally want to know

- o How to describe the flow in various areas of pipe in terms of velocity, pressure, pressure drop, turbulence, and the particle and fluid element's physical characteristics,
- o chemical constituents of each phase.
- o mass transfer of all phases described separately and as a whole.

Second: We get the information through sampling, but have problems because

- o all sectors of the pipe are not the same
- o nonisokinetic traverses of pipe don't give reliable information on mixed flow
- o total flow measurements (Weber Separation, etc.) give information on mass flow, but the conditions in the pipe must be deduced from results after separation.

Sampling Strategy For Multi-Phase Flow

Sampling Location

A location should be chosen such that changes in the fluid composition are minimized. This includes prevention of contamination by and reaction with materials other than the well fluid, as well as prevention of changes in the physical states of the various phases in the fluid, including pressure and temperature changes that would affect solubilities and reaction rates.

To meet those requirements, the best location to sample from would be downhole, if the goal is to determine the characteristics of the fluid entering the well bore. However, that location is also the most difficult due to extreme physical conditions of temperature, pressure, and flowrate. Also, the inaccessibility of that location delays sample retrieval and subsequent preservation.

If it can be assumed that the fluid phases are thoroughly mixed in the vertical well column, then a representative sample could be obtained by lowering a sampler that would allow a relatively undisturbed flow both through and around it before being "stoppered." Subsequently, the sample container must be maintained at sample collection conditions until removed and analyzed. The latter requirement alone makes this procedure a doubtful choice.

The next best alternative for obtaining a representative sample is at or near the wellhead. This location is preferred for accessibility over downhole locations and for minimizing fluid changes over alternative downstream locations.

Sampling Port

The port should allow access to all volumes of the pipe likely to contain different flow patterns, chemical compositions, or physical states. This would seem to require a pair of ports located at a 90° angle on a cross section of the pipe (especially if the pipe is horizontal) or else a "porcupine" arrangement of ports in order to confirm the presence or absence of those dissimilarities.

The ports should be constructed of materials and with a design such that they do not produce chemical or physical state changes in the fluid at the sampling point.

Safety features should be such that the sampling personnel are not exposed to the well fluid, excess heat, or noise or to potential equipment problems such as uncontrolled ejection of a probe from the port.

Well Conditions

If the objective of sampling is to obtain the most representative sample of well fluid under "typical" producing conditions, the well must be allowed to flow at capacity and for a sufficient time before sampling to insure steady-state conditions. Sampling should be conducted over as short a period as feasible to minimize the effect of possible well fluid changes that are a function of time.

Equipment

Three ways to obtain representative samples of a multiphase flow system are to instantaneously extract a cross sectional sample of the flow (difficult under geothermal conditions), sample isokinetically at various points across the pipe, or throttle the flow to achieve single phase flow and sample appropriately. If isokinetic sampling (IKS) is chosen, volumetric flowrates must be determined at each sampling location using pitot tubes or other velocity measuring devices.

Required Accuracies Of Sampling Methodology

The accuracies of the sampling technique will be determined by the final accuracies required on the analyses by EPA and the base line amounts that exist in the wellhead. For example, elements such as chlorides that exist in large amounts may be sampled in a relatively crude way while such things as boron, etc., may require a more delicate technique.

Reproducibility of Results

Perhaps the most critical aspects of any multiphase sampling methodology is that the system deliver a sample that is both reproducible and representative of the flow field. The absence of these critical elements that exist in many current techniques makes it impossible to differentiate nonuniform distributions of brine and steam in the flow from a nonuniform sample being delivered to the sample probe. Representativeness in sampling is greatly affected by the rate at which the sample is withdrawn from the system. Ideally, it should be withdrawn at a rate equal to the localized flow rate. A rate that is faster or slower than the local rate gives a nonuniform sample:

- Faster sampling rate yields a sample that has proportionally more steam.
- Slower sampling rate yields a sample that contains more brine than steam.

To ensure reproducibility, the sample must always be withdrawn at the same rate. Interestingly, the act of sample withdrawal precludes the possibility of seeing high frequency variations because it takes a several seconds (as a minimum) period over which to obtain the sample; in fact, all techniques provide a time-averaged sample.

Finally, the first step in sampling is to determine, "What do I want to know?" and "How well do I want to know it?"

In species and particle-size distributions and gas partitioning, you must use an IKS system to ensure representative and reproducible samples.

It may be of use to establish baselines using IKS and then to develop a national approach to compare it to other simpler techniques which can be used in the field for periodic compliance monitoring.

Sample Preservation

Much experience in sampling, as far as geothermal work is concerned, has been confined to the Geyser area in northern California. From this work, it was concluded that whatever sampling analysis that can be accomplished onsite should be, especially in the area of gas analysis. Two major problem areas were noted:

- Sample degradation.
- Not being able to reproduce results after leaving the site.

The primary concern has been in H_2S analysis where samples have changed too quickly to be removed from the site. The best results were obtained by not separating the liquid or gas phase but capturing the sample in a single phase using ammonia hydroxide and back titrating with silver nitrate. The method has gained more acceptance among the air pollution districts concerned than the calcium sulfate iodometric method stated in the EPA Guidelines.

Onsite gas chromatography has been used to trace oxygen in the system to avoid unnecessary sample contamination while being able to sample more frequently. There are some items that do not lend themselves to field analysis and therefore should be preserved and sent to a laboratory. Sample preservation depends on the chemical constituent being tested, whether it can be readily tested in the field and the conditions encountered.

Effects of Solids

Most geothermal power plants must be designed with scale control in mind. Therefore, the scale-forming minerals must be measured accurately. Unfortunately, solids in the flow, and solids which deposit upon the sampling apparatus, can destroy the accuracy of these measurements. The sampling probe can get covered with scale; the sample may include sand particles which serve as nucleus for calcium carbonate crystals. Unfortunately, (if the solids are simply filtered out and disregarded) such samples can easily give very inaccurate measurements of the scaling potential of the brine.

A standardized time-integrated method for dealing with solids in multiphase flow must be developed. Sampling techniques which allow a probe to get "covered" with scale must be changed to give results which adequately measure the chemical constituents of the brine.

DEFINITION OF RESEARCH NEEDS

Sampling Hardware

Sample Port Design

Research seals to allow probe to enter fluid stream and traverse without contaminating fluid (not too critical if port downstream of sampling nozzle), in safe manner for user, and in reuseable manner.

Probe Design

- o Purpose
  1) Collect representative phase fractions at each of various traverse points across flow stream.
  2) Collect grab sample of total flow.
- o Isokinetic
  1) Material -reactions/contamination.
  2) Probe shape-(a) Location of sample collecting nozzle vs velocity/pressure differential measurement location (b) Size of probe vs pipe to be sampled (c) Necessity of matching T&P after sample enters probe.

3) Is there any requirement for pumping the sample?

4) Measurement of sample flowrate

- Grab Sample

Is there a way to quickly seal off and rotate out of a flowing pipe a grab sample using a "ball valve" arrangement that seals both ends of a section of the pipe simultaneously?

Collection Train

- Location of filter (heated or not, material) vs phase separator vs impinger train/absorber.
- Pressure/temperature requirements of train--where do you cool (heat?), allow a pressure drop, etc.?

Flow Measurement Devices

- Pressure differential devices (pitot tubes)
- Venturi devices
- Mass flow meters

Fluid Mechanics

In considering the fluid mechanics aspects of two-phase flow, we must take into account reliable predictive models that describe the multiphase flow in and between various regimes. We must also consider chemical partitioning, nucleation, and the perturbation of flow by the sampling probe.

Sample port location

- vs flow disturbances
  1) Existing engineering data on two-phase
- vs flow regime
  1) Vertical
  2) Horizontal
  3) Diagonal

  } if only one port, vertical probably desirable
- Horizontal or vertical pipe

Flow field

- Choices
  1) Total flow
     a) Flash, condense and recombine to liquid and noncondensible gases

b) "Total sample"
- o Recombine to single phase
- o Condense everything

2) Traverse flow (slipstream)

Sampling considerations

- o Effect of sample probes on flow field
- o Effect of sample withdrawal on flow field (isokinetic)

Recommendations

Fluid mechanically speaking, the ideal sampling two-phase situation would be on the 10-inch production line 100 pipe diameters downstream and 50 pipe diameters upstream from the nearest flow disturbances. If one is confined to only one sample port, it should be vertical to the field. However, the ideal situation would be to have ports mounted to permit vertical, horizontal and diagonal traverses of the field. Finally the ideal way to sample the system is isokinetically because of its virtues which are:

- o Truly representative sample in the following parameters:
  1) Chemical
     a) solids
     b) partitioning
        - o gases
        - o speciation
  2) Physical
  3) Thermodynamic
- o Reproducibility under same flow conditions

Chemical Concerns in Multiphase Sampling

There are many chemical concerns in analyses of geothermal brines, but only two types of concerns are specific to the problems of multiphase sampling. These two concerns can briefly be described as--

- o Flow oriented
- o Chemistry oriented

Flow oriented concerns include the problems of sampling wells which will have different chemical constituents depending on the flow rate, flow history, and well history. This leads to a sampling concern because chemical sampling reproducibility is affected by these parameters.

Chemistry oriented concerns include the problems of representative sampling of precipitating solids. Scale-forming minerals frequently precipitate and are carried along with the flow, not necessarily in a well-distributed manner. Flow-integrated samples must be taken to adequately sample these particulates. Similar concerns are possible in sampling noncondensible gases. These gases actually partition between a gas phase

and solution in water. The partition depends on the pressure, temperature and chemistry situation in the well and the pipe, and can influence the chemical analysis accuracy.

Policy Guidelines

- o Research Sampling
- o Compliance Sampling

Policy Guidelines can be broken into two categories. The first category pertains to the gathering of research information, which would be limited to the gathering of base case information. This set of guidelines would be broader in scope than those related to compliance because they would be based in pure research. The second category, compliance guidelines, would be set after the base case had been established. Frequency, cost, simplicity of method, and accuracy of sampling would vary between compliance and research. The broader scope of research sampling would multiply some of the points mentioned above. Research sampling might not be more frequent than compliance but in most cases would be more detailed, cost more, and demand more accuracy. Research sampling would naturally include more experimentation which would later apply to the compliance case.

Use of Techniques Appropriate to Purpose of Sample

- o Research is detailed and notes changing of well
- o Compliance is simple, frequent, low cost
- o Regulations should reflect fact that well contents change over time.

Research must be initiated before compliancy testing. The guidelines must be established which would include a much more comprehensive program using all the other four points: (1) description of multiphase flow, (2) evaluation of sample hardware, (3) application of techniques, and (4) development of new techniques. Once you have found out the extremes or variables in a given research test program (e.g., ambient air standards from monitoring strategies to establish what levels of pollution will be tolerated for (natural existing levels) H_2S), then you can proceed to limit any increase above these levels from drilling wells, wellhead bleeds, and power plants. Compliance would consist at this point in making sure that emissions from old and new equipment do not exceed these limits.

STRATEGIES FOR STANDARDIZATION OF SAMPLING METHODS

Physical and Chemical Description of Multiphase Flow

The most critical aspect of any multiphase sampling methodology is that the methodology must deliver samples which are both reproducible and representative. Since the chemical nature of the samples is effected by the flow regime through the partitioning which occurs in going from single to multiphase, we must be capable of describing the partitioning of chemical species and how the hydrodynamic regime effects the partitioning.

Currently our ability to describe the partitioning of chemical species between various phases in multiphase flow is limited. Since equilibrium is seldom attained, we are forced to consider the kinetics of the partitioning mechanisms which in turn are highly dependent on the flow field. The partitioning of various elements in turn then causes or rather indicates nucleation of new phases and/or causes the disappearance of old phases. All of these effects determine the chemical composition of the system at a point in time and space. Hence these effects, and our ability to predict them, determine our sampling strategy.

Research would need to be centered first on the equilibrium partitioning reactions and rapidly evolve into the kinetic mechanisms involved in the partitioning. Once the various kinetic paths are defined, the effects of the hydrodynamic regime on the chemical kinetics should be investigated. Using all of the above data, predictive models can then be constructed. Nucleation phenomena related to the formation of liquids/gases/and solids in a multiphase flow then need to be quantified and then these models combined with the partitioning models.

Evaluation Of Sampling Hardware Technology

Choice Of Materials For Use In Port/Probe/Train

- For general (research) type hardware, assure the best compromise based on knowledge of reactive chemical species present.
- Set up "controlled" environment (i.e., an actual well that has been "adequately" characterized) and build first generation sampling devices from different materials and determine effect of material on sample composition.
- For more specific (compliance test) sampling systems, material need only be nonreactive to specific groups of substances being monitored at that time.

Flow Characterization

Using a well known (artificial?) flow system, compare the ability of various flow sensors (pitot tubes/rotating elements/vortex sensors, etc.) to measure that flow as well as to determine pressure and temperature at each measurement site (if essential). Phase distribution in terms of gas and liquid relative volumes and patterns of distribution are used in definition of flow regime.

Probe Comparisons

- Using a single well whose fluid flow and composition are relatively stable and understood, perform simultaneous (or near simultaneous) sampling tests using various probe designs.

- o Develop rating criteria to evaluate performance of candidate probes.

Sampling Train (downstream from probe) Comparison

Similar to "Collection Train," except using a single probe design followed by various train systems (i.e., total flow absorption vs separation of phases followed by absorption)

NOTE: Tracers could be injected into the well flow prior to the sampling point in order to help evaluate the various systems. The tracers might be totally foreign material or else spikes of chemicals already present.

Applications of Techniques to Environments

Locations

- o Physical locations in system
  1. Drilling
     a. Gas releases etc. (blooey line)
  2. Production Locations
     a. Wellhead (production line before separator)
     b. After separator
        (1) Brine lines
        (2) Steam lines
     c. Cooling tower
     d. Injection and monitoring wells
- o Sample port locations in release areas
  a. Vertical--recommended if single port is used
  b. Horizontal
  c. Diagonal

Techniques

- o Physical Specificity
  1. Flow rate
  2. Flow time and sample time
  3. Probe type — flash and
  4. Sample train type — condense or condense
  5. Area of flow field sampled
  6. Other conditions as needed for individual components
- o Chemical Specificity
  1. Sample train chemicals
  2. Sample preservation

LIQUID SAMPLING

The Liquid Sampling Workshop identified several topics of concern within two major categories:

- o Issues
  - Definitions
  - Procedures
  - Evaluations
  - Special Techniques

- o Recommendations
  - Sample Collection/Treatment
  - Process By-Products/Holding Pond Tailings
  - Direct Release Into Surface Water
  - Effects of Dissolved Oxygen
  - Closed Loop Injection
  - Cold Water Injection

ISSUES

Effluent Definition

Three general categories of effluents

- o Resource supply--The geothermal water supply system. Examples: Hot Wells, Hot Springs, etc.

- o Resource conversion--Utilizes the heat in the geothermal water. Examples: power plant, food processing, space heating, etc.

- o Release Point--Point at which the geothermal water is disposed of. Examples: injection wells, evaporation ponds, release to streams, etc.

Types of samples needed

- o Samples to furnish information for research and engineering applications.

- o Samples to furnish information for regulatory purposes.

Types of samples to be collected in the three categories of the geothermal complex.

- Resource supply--Samples collected at this point would furnish information for reservoir and resource conversion engineering. These samples would furnish information on reservoir changes that would impact the resource conversion unit and the effluent at the release point.

- Resource Conversion--Samples collected at this point would furnish information for resource conversion engineering. Effluent treatment would take place at this point to control certain species (chemical) at the release point.

- Release points--Samples collected here would furnish information for resource conversion engineering, effluent injection technology, and for regulatory purposes.

Site specific requirements would consider the following:

- Each resource area has problem chemical species. Examples: high mercury, arsenic, salt, etc., concentrations that may not exist in the other areas. Sampling techniques would have to be applicable to that need.

- Resource conversion methods would determine sampling requirements.

Procedures

Overview

- Standardized sampling does not exist.

- Standard definition for liquids (intercomparison) (Defined to a standard P&T).

These two topics are broadly interrelated in that the choice of methods by which a sample is extracted from the system defines, by virtue of the individual plumbing, what is reported as a liquid sample. This problem can arise both in one-phase or two-phase systems. A two-phase system must be sampled, separated, and quenched at a specific pressure and temperature, and these conditions recorded, to evaluate the nature of what is called liquid. A one-phase system must not be allowed to flash with consequent separation of phases prior to quenching of the liquid sample.

A liquid sample at the point of collection (i.e., where placed into the sample container) could be defined as one obtained by cooling to ice bath conditions in a condensing unit. The practicality of standard pressure can be addressed by recording barometric pressure in the condensing unit and in the atmosphere. Any practical use of analysis of such a sample should not be questioned.

The sampling of a two-phase/one-phase system will probably always (to a degree) be a problem of selective partitioning of the sample at the sampling point. This has been a problem with isokinetic samplers which supposedly

sample statistically across a two-phase/one-phase flow and even more so with sample valves placed on the top, bottom or sides of a two-phase/one-phase flow line. Sample ports placed in zones where two-phase/one-phase are supposedly thoroughly mixed, appear to show variability which is a function of both sample valve diameter and the degree to which a sample valve is opened.

This problem appears to be addressable by either of two approaches: (1) standardize sampling tubes and ports as to size and design, plus control of P&T drop prior to entering the condensing or separation system; or (2) sample liquids of concern at points in the process system that are near the potential points of effluent. This will, in the first case, minimize phase separation, and in the second case, allow handling of cooler fluids, again minimizing the problem.

From the viewpoint of release of pollutants to the environment, any of the problems in sampling may be of a lesser magnitude than requirements for engineering or reservoir evaluation purposes. Assuming normal operation of a geothermal power conversion unit, liquids produced at the separator (line) and liquids produced from steam generator (condensate) are the largest potential effluents. Catastrophic release-blow-out-pipeline failure would probably have a greater impact by virtue of 500^{0}F water release than by chemical pollution and should probably not be addressed as a normal chemical pollutant source.

The volumes and concentrations of brine and condensate are more easily measured at point of discharge where lower P&T prevail. Thus for effluent monitoring purposes, it is recommended that sampling strategies be tied to the actual points of discharge. This also has the advantage of avoiding the need to assume partitioning ratio functions for constituents in wellhead liquids that would be flashed in process use.

The goals of recommendations in this area must then be:

- Agreement as to point of sampling
- Agreement as to type of sampling ports
- Agreement as to P&T conditions of sampling and practical records required to characterize samples.
- Recording of P&T and flow rates of system for future reference.

Reporting Criteria

Scientists and lay people are always faced with substantial uncertainty in reading chemical analytical reports. A list of the chemical analyses with a minimal sample location is not sufficient. Chemical analyses should be accompanied by the following ancillary data:

- Time-date of sample
- Barometric pressure--ambient temperature
- Sample size

- Number of samples
- Preservation techniques
- Delay time between collection and analysis
- Construction materials/constraints
  - Orifice size
  - Elbows, reductions, restrictions, etc.
  - Material type, i.e., steel, copper
  - Specific sample location

- System configuration diagram
- Sample configuration diagram
- Unusual circumstances or conditions during sampling
- Duration of flow test before sample collection
- Rate of flow

These data lend credibility to chemical data. A systematic presentation of sampling conditions allows for tests of reproducibility.

Unit standardization

Readers of chemical analyses are frequently confounded with a vast diversity of chemical units of measure. Analyses should be displayed in S.I. units. The use of one standard unit of measure for water will lend uniformity and ease of manipulation of data . The use of more specialized units such as milliequivalents per liter, (millimoles) per liter, etc., facilitate certain tests and interpretive methods, but are more generally difficult to utilize for general interpretations.

Sample Reproducibility

Nature is generally very uniform within a large statistical sample. Many scientific measurements ignore the statistical nature of data. Water samples taken from natural sources, i.e., hot springs, cold springs, fumeroles, etc., show significant variability over relatively short periods of time. Constituents in effluents from artificial sources, i.e., steam wells, also exhibit variability. Reproducibility is dependent on sampling technique and analytical technique but it can only be ascertained by repeated collection and analysis. Analyses should always be accompanied by notations describing the number of samples taken per discrete sampling period. Samples should also be taken at specific time intervals spaced evenly throughout flow tests. Reports should include at least a minimum of statistical tests, i.e., standard deviations, etc.

Evaluation - Liquid Sampling

Definition of Major Issues:

Sample history - Obtaining and reporting data that describes the conditions under which the sample was collected; providing spatial and temporal information that will enable the user (of the sampling and analysis results) to make meaningful comparisons.

Incomplete or missing sample history data frustrates efforts to determine whether that sample represents normal, infrequent, accident or upset conditions and, if it is, under what circumstances it could be, reproducible.

Sample collection point - Determining the proper location (in space and time) at which a sample should be collected to yield data pertinent to the purpose behind the sampling effort.

Sample preservation and permissible retention time - Specifying techniques for sample preservation germane to the type of material collected and constituents to be analyzed. Adequacy of preservation techniques will dictate the permissable time lags between collection and analysis and, hence, the potential need for on-site analyses.

Illustrations of Importance of Issues:

- Sample History Sampling point (chain of evidence): Flow or process diagram with sampling points shown is required for knowledge of sampling condition. An example, as related to the constituents, is the addition of additives and what effect that might have on the sample. Pipe expansions can allow flashing, therefore, any pressure drops should be identified. An example is that with pipe expansion, calcium carbonate scaling will occur in certain resources and results down-line will show less calcium present in the sample.

- Sampling preservation and retention time: On site analysis is dependent upon sample preservation. Dilution to prevent silica precipitation is an example of sample preservation. Stabilizing solutions are also used for sulfides. Specific attention must be given to sample preservation which is an area where further development and research is required. The allowable sample retention time is directly related to the capability to preserve the sample.

- Vacuum filtration should not be used where volatile or significant pH changes can occur allowing either loss of sample constituents or precipitation.

Special Techniques

One special technique is the installation of conductivity probes, pH probes, CO_2 probes, dissolved oxygen probes and selective ion probes (Cu, Ph, Hg, CH, NH_3) which would be coupled to automatic data recorders. In addition, sampling pumps attached to automatic analyzers such as the "Technicon" type unit could be utilized to develop and maintain baseline or characteristic values at each individual location, which then could be compared to individual "grab" samples.

Effluents which have cyclical values in certain periods could then be given time weighted averages, by a regulatory agency, as opposed to a single sample at a certain high point which would cause rejection or plant shutdown.

This form of sampling would be very similar to the Hi-Vol air sampler utilized in monitoring particulates in air quality studies, and which also gives time weighted values that are more representative and are accepted as the proper manner of evaluating samples which may fluctuate.

RECOMMENDATIONS

Sample Collection/Treatment

Introduction

Sample collection and treatment are of fundamental importance in obtaining quality chemical analysis. Geothermal effluents contain high concentrations of notably unstable species. Geothermal fluids are especially subject to the problems of suspended solids, chemical precipitation and degradation prior to analysis. These problems are magnified as the *in situ* temperature-pressure conditions diverge from standard conditions. The topics of filtering, preservation, sampling vessels and transportation, and storage are briefly treated for total dissolved solids and the following elements: arsenic, barium, boron, cadmium, chloride, chromium, fluoride, iron, lead, lithium, manganese, mercury, selenium, silver, and zinc. These elements are of concern as potential pollutants in geothermal effluents.

Filtering

The presence of suspended solids significantly degrades various chemical techniques, especially spectrophotometric analytical methods. Suspended solids are especially prevalent in geothermal well fluids because of the extraordinary physical and thermal abrasive qualities of the subsurface environment. These solids can best be removed by filtering.

Natural effluents are to be filtered through a 0.45-micrometer filter. A number of excellent commercial filters, filter holders, and related apparatus are available. The U.S. Geological Survey publishes several documents describing filtering techniques and procedures for various conditions and situations.

Sample Collection and Preservation

The chemical nature of various species and media requirements for various analytical techniques beg a diversity of sample containers and preservation techniques. Certain elements may precipitate or coprecipitate as stable compounds as temperature, pressure, eH and pH conditions change drastically from the subsurface conditions. These elements require preservation.

Addition of high purity reagent grade nitric acid is the most widely accepted preservation technique for water. The sample pH is thereby lowered to pH 3 or below. Many less popular techniques are also available. Acid preservation should be used exclusively for the sake of uniformity. The following elements should be analyzed from an acidified aliquot of filtered sample: arsenic, barium, cadmium, chromuim, iron, lead, lithium, manganese, silver and zinc.

Preservation is not required for boron, chloride, fluoride and selenium. These elements may be analyzed in a second unacidified filtered aliquot.

The determination of total dissolved solids (TDS) requires preservation by dilution because the addition of any preservative can contribute to the TDS. Dilution is an effective deterent to precipitation. A one-to-ten volumetric dilution of sufficient volume should be made from a third filtered aliquot. Large volumes may be required when gravimetric techniques are employed.

Mercury in water may be difficult to preserve. It is recommended that mercury be analyzed on site from a fourth unfiltered, unacidified aliquot.

Vessels

Glass containers with polyseal caps should be used. Glass does not absorb ions in the fashion of certain porous plastic materials, i.e., polypropylene. Also, changes in sample coloration and precipitation can be observed, where as most plastic substances are translucent or opaque.

Special Conditions

Certain geothermal fluids suffer immediate precipitation during the necessary pressure-temperature reduction required during sampling. In this situation, acidification of the unfiltered sample could potentially contribute ions from the entrained suspended solids. Acidification of even slightly turbid samples should be avoided. In this case, a one to ten dilution of sufficient volume should be made from unfiltered samples before significant precipitation occurs. This dilution must be used for all determinations.

Transportation and Storage

Water samples should be transported to analytical facilities as quickly as possible. Long delays before analysis will result in sample degradation. Samples should be kept as close to standard temperature as possible. Samples should be kept in a dark environment and should be subjected to minimal agitation.

Conclusion

The unique nature of geothermal effluents presents the technical community with several unusual chemical and physical problems. The chemical and thermal character of some geothermal fluids requires specialized sampling techniques. High quality chemical data can be obtained only when the aforementioned collection and treatment techniques are uniformly applied.

Sampling Procedures For Process By Products and Holding Pond Tailings

Introduction/Release Point Definition

This section discusses sampling procedures for those liquid and liquid/solid matrix effluents which are not discharged directly to a natural water

body or reinjected into the geothermal reservoir. These are effluents, then, which are subject to land disposal.

The regulatory impact on geothermal effluents of this nature will occur principally through the Resource Conservation and Recovery Act (RCRA). Sampling programs will have to be conducted to (1) identify the chemical characteristics of these effluents in order to determine how they are to be regulated, and (2) provide data needed routinely to ensure that proper transport, treatment, storage, and disposal methods are employed.

The types of effluents arising from release points under the heading of process byproducts and holding pond tailings include the following:

- Resource Supply
  - -drilling muds
  - -reserve pit material
  - -brine pit material
- Resource Conversion
  - -sludges from steam separators
  - -cooling tower sludges
  - -sludges from H_2S abatement systems
  - -bottom material from cold water injection cooling ponds
  - -clarifier and other preinjection particulate removal system sludges

Not all of the above effluents will necessarily be present at a particular geothermal installation. Further, the matrix in which an effluent occurs and its chemical composition will be highly site-specific. Accordingly, the procedures discussed below must be considered as guidelines subject to modification by site-specific factors which may significantly affect a sampling program.

Statement of the Problem

Geothermal exploration and development activities generate a number of effluent streams which may be disposed of on land. These effluents will eventually become regulated under RCRA. Sampling will be necessary to characterize the effluents to both facilitate regulations development and ensure compliance once the regulatory framework is adopted.

Collecting valid and reproducible samples of geothermal effluents subject to land disposal will encounter difficulties due to a number of factors including--

- Wide fluctuations among resource areas and within any single reservoir over time which may significantly affect sample chemical composition
- Occurrence of effluents in a variety of matrices (e.g., reserve pits which may contain drilling muds, well cuttings, oils, and brines)

which make selecting the specific locations and number of sampling points critical factors in determining sample representativeness.

- Uniqueness of each conversion facility in terms of fluids composition, pollutants of concern, heat extraction methods, pollution control systems, etc., which collectively impact the number, volumes, and composition of the effluent streams.

Sampling Techniques

Sampling techniques will vary according to the matrix in which the sample is to be obtained. For the types of effluents under consideration here, three distinctions can be made:

- Samples of storage piles or containerized materials
- Samples of settled material in tanks or basins (e.g., cooling tower).
- Samples from pits, sumps, and holding and evaporation ponds.

For each of the above, a discussion is presented below of the following:

- Sampling equipment and methods
- Number and location of sampling points
- Sample storage and preservation
- Reporting data requirements

Storage Piles and Containers

1) Equipment and methods

Equipment needs will vary with the volumes, geometry, and degree of solidification of the material to be sampled. A hand scoop may be sufficient for relatively small piles. For large storage piles, a shovel will be needed to penetrate the surface to obtain samples at depth. A rockhammer may be necessary for well-compacted material.

2) Sampling points

A composite sample should be collected. The number of subsamples to be included in the composite will be determined by the size and apparent consistency of the material. Surface, mid-depth, and bottom subsamples should be collected where material depths exceed a meter (a few feet) and partitioning is evidenced by an exploratory hole. Material stored in piles encompassing large surface areas should be sampled at a minimum of four points equidistant along the perimeter and at two points near the center. Access restrictions may necessitate modifying these procedures.

3) Storage and preservation

Samples should be collected in 3.8-liter (1 gallon) widemouth polyethylene bottles. Glass bottles should be substituted when analyses for organic constituents are anticipated. After filling, the sample bottle should be tightly capped and taped.

Preservation via addition of acid or other media is difficult for sludges and similar liquid/solid matrices. Freezing has been employed, but its effects on sample chemistry are not well known. Initiation of analyses as soon as possible is the preferred approach. If samples are to be retained beyond 24 hours prior to analysis they should be refrigerated at 4°C.

4) Reporting

Data to be reported should include the following:

- Time/day of sample collection
- Number of samples collected and sample size
- Sample compositing methods
- Preservation techniques
- Physical dimensions and composition of the storage pile or container
- Diagram showing the location of the sampling points
- Identification of the process from which the material was generated (via a process flow diagram if available)
- Indication of whether the material sampled is generated on a continuous or batch basis
- Description of any recent physical disturbances to the storage pile, particularly any that are weather-related (e.g., rainfall) in the case of outdoor storage
- Unusual circumstances or conditions encountered during sampling
- Use and description of additives

Settled Material in Tanks or Basins

1) Equipment and methods

The depth of overlying fluid and the degree of compaction of the settled material will affect the selection of sampling equipment and methods. Shallow tanks or basins containing bottom material not readily re-entrained in the overlying fluid may be sampled with a hand shovel. Compacted material at

depths of a meter (several feet) or more may require use of a core piston sampler. An open mouth sampling bottle with extender or a dredge may be employed for readily re-entrained material.

2) Sampling points

A composite sample should be collected consisting of at least four subsamples taken equidistant along the perimeter of the basin tank bottom. Several samples along the center axis should also be included if access is possible.

3) Storage and preservation
(See above under "Storage Piles and Containers")

4) Reporting

In addition to the data specified above under "Storage Piles and Containers," the flow rate of fluid into the basin or tank should be reported.

Pits, Sumps, Holding and Evaporation Ponds

1) Equipment and Methods

Equipment needs may include any combination of the devices described under "Storage Piles and Containers" and in paragraph 1 above. Selection of equipment and sampling methods will be highly site specific and rely on the judgement of the sampler. Important site specific factors include the following:

- Physical dimensions of the pit sump, or pond (i.e., surface area, depth)
- Access considerations: Is a boat or catwalk available? Can the surface be safely walked on? Do steep or unstable sides inhibit perimeter sampling?
- Apparent composition (e.g., pond with standing water and settled bottom material, sludge lagoon, stratified liquid/solid matrix).

A large pond with standing water may be accessible by boat and the bottom material obtained via core piston samples or dredge, depending on degree of compaction. A shallow pit containing well-mixed sludge may be sampled from the perimeter using an open mouth sampling bottle with extender. Drilling operation reserve pits containing random mixtures of muds, cuttings, oils and brines may be sampled by digging 0.3-meter (1 foot) diameter holes with a hand shovel or posthole digger and collecting a vertical cut sample.

For obtaining liquid samples in cold water injection cooling ponds, an evacuated type water sampler that can extract segregated samples at various depths may be used.

2) Sampling Points

A composite sample should be obtained which consists of subsamples taken at representative horizontal and vertical plane locations (the latter only if the depth and partitioning of the material so indicates). The number of subsamples needed will vary according to the sampler's assessment of the homogeneity of the pit, sump, or pond material. Four equidistant perimeter samples and two center axis samples (if access permits) should be collected as a minimum. Near surface, mid-depth and bottom samples or a vertical cut sample should be obtained at each point if the material is more than 0.3-meter (1 foot) in depth and apparently partitioned.

3) Sample Storage and Preservation

(See above under "Storage Piles and Containers")

4) Reporting

In addition to the data specified above under "Storage Piles and Containers," the following should be reported:

- For drilling operation reserve pits,

  -types of muds used
  -if geothermal reservoir was contacted
  -date of last drilling and flow testing

Conclusions/Recommendations

Geothermal exploration and development activities will generate liquid/solid matrix effluents requiring land disposal. These effluents will become regulated principally under RCRA. Sampling will be necessary to establish the proper regulatory framework for these effluents and ensure compliance with treatment, transport, storage, and disposal regulations.

The experience base for sampling these geothermal effluents is not large and protocols are not well established. This situation is exacerbated by the strong influence of site-specific factors on sampling procedures. Heavy reliance on the discretion of the sampler in the field to develop appropriate procedures will have to be tolerated. Hence, comprehensive reporting of the sample history will be critical if the results obtained are to be meaningfully compared with other data.

A particular need for further research is in the area of sample preservation. The effects of various composition containers, freezing, and substitutes for traditional acidification are not well known for sludge-like samples.

References

"Field and Laboratory Sampling and Analysis Manual for the Presurvey of Solid Waste Management Practices in the Mining Industry," Draft Final Report,

prepared by PEDCo Environmental, Inc., for the US EPA/IERL-Cin., January 1980.

Direct Release of Effluent Geothermal Fluids into Surface Waters

This section deals only with spent geothermal fluids which are to be released directly into lakes, ponds, streams or rivers. The term "direct" may in some instances include temporary passage into a cooling pond or water treatment pond prior to actual discharge into the natural body of water. The discussion is perhaps pertinent primarily to the lower temperature, direct utilization geothermal projects. This section will discuss the methodology of sampling and the location of the sampling points.

The problem encountered in this area is the nonuniformity of these project constructions and so the unestablished procedures required for results of analyses to have some validity and uniformity. This discussion would hopefully assist in the formulating process of standard methodologies in sampling for geothermal systems of this nature.

The existing techniques in existence are for the most part entirely acceptable. The main concern being that all individuals standardize on the location the sample is to be obtained and also the container material and method of preservation.

For discharge directly into the surface water it is assumed that the effluent is at a temperature no greater than 32°C (90°F). If the temperature is greater than this, the effluent will be entering an initial cooling pond. The water to be sampled must then be analyzed at the point of discharge in the pipe, case 1 32°C (90°F or less), in such a manner that there is no exposure to the air prior to obtaining the sample. The most acceptable manner for performing this is by way of installing a tap in the top of the pipe. If the pipe is flowing full capacity and is not exposed to the air, it may be located right next to the discharge point. If however, the pipe is open to the air and flowing only partially full, the tap must be located at the point where the pipe is still maintaining full flow. The water is then allowed to flow into the collection bottle to thoroughly flush the container, rinsing out all traces of air and any other surface contaminants that may be present. The sample container may then be preserved and sealed as necessary.

In the event that the temperature is greater than 32°C (90°F) and a cooling or treatment pond is required, the sampling point should be at the point in the pond where the liquid effluent exits via the pipe or weir. If it is via a pipe, the sample should be collected from a tap as discussed in the previous paragraph. If the effluent exits via a weir or open channel, the sample to be collected should be obtained by submerging the container in the stream flow and obtaining in an acceptable manner.

Case 2 may result in the need for sampling of bottom sediment or sludge as the case may be. The sludge-sampling procedures are discussed elsewhere in this text and should be followed as necessary.

The sampling containers are the same as those recommended by the entire group, glass with polyseal lids for all but the silica which is to be plastic

preferably teflon or polypropyplene. The size of the sample is to be determined by the individual analyst and the analytical techniques to be utilized.

The preservation of the samples will be much the same as those recommended by the EPA for its "Water and Wastewater" analytical techniques. High purity HNO_3 for all the constituents requiring preservation with the exception of F and Cl T. The number of individual samples to be collected will again depend on the analytical technique to be employed.

In as much as possible, it is believed that acceptable techniques do exist for most sampling of the lower temperature geothermal fluids, and it is merely a matter of conforming to acceptable practices whenever possible.

The main area of concern is that everybody does the process of sampling in a uniform manner, thereby producing uniform data.

Effects of Dissolved Oxygen On Geothermal Water

In general, surface water, because of air exposure, is saturated with oxygen. As this water percolates through the soil most of the oxygen is removed by biological reactions with plant life. Any remaining oxygen will be removed by chemical action as the water travels through the soil and rocks to the aquifer systems. As the result of this biological and chemical purge, most ground water is oxygen free. This is especially true in the deeper geothermal aquifers.

Water in the geothermal aquifers relative to geologic time is never in equilibrium due to the cooling of the rocks in the system and the exposure of the water to different rocks and minerals as it travels through the aquifer. However, within the short time of man's involvement with a particular aquifer, the water can be considered at equilibrium with its environment. Understandably, anything changing this environment will impact the delicate equilibrium of the water system. For example, the pressure changes and the exposure of the water to the well casing during pumping will shift the equilibrium of the water system. Saturation of this complex system with oxygen will certainly cause chemical reactions and interactions that will result in major equilibrium shifts. Studies of the impact of oxygen saturation on ground water samples should be considered to determine if major changes take place. The results of the study could play a significant role in the design of sampling systems in a geothermal resource conversion unit. It would help in the evaluation of the integrity of chemical data from water samples.

Closed Loop Injection

Introduction

The closed loop injection for disposal of liquids from a geothermal process system will be a common means of disposal both in low temperature and in high temperature geothermal applications. Sampling these waste liquids to monitor their potential impact on the zone of injection will range from a

negligible problem to a potentially difficult problem depending on the enthalpy of the waste liquid.

In the low temperature cases, (TC boiling) physical sampling problems will be minimal and sampling will center on the normal concerns for representative sampling that occur with any industrial effluent that would be introduced to the environment via disposal wells. Unless a particular site-specific potential pollutant requiring unique preservation techniques is identified in baseline studies of the reservoir field, existing regulations for fluid disposal should not need to be modified, i.e., geothermal liquid disposal is not a unique case.

In the high temperature case, where boiling of a liquid effluent is likely to occur upon sampling, adequate sampling techniques should be established to ensure that all identified potentially hazardous constituents are representively sampled. The potential problems in this sampling arise when phase separation occurs, volatile species are partitioned from the liquid phase, and a non-representative sampling is obtained. It should be emphasized that samples biased in this fashion may either over-emphasize or underestimate the impact of a potentially hazardous species depending on the direction of phase bias upon sampling.

A unique feature of liquid wastes from a geothermal process system, aside from physical sampling problems, is the potential variation of effluent composition through time which may occur as the result of both variations in operation modes of a power plant, and as a result of changes in the produced resource base. From an environmental viewpoint, these variations may be negligible. However, there is compositional variation between wells in a field, the produced fluids in a given well are likely to change with time, and changes in steam separator P&T conditions will change partitioning functions for some species. Liquid waste monitoring programs may have to address some of these issues when site-specific monitoring is designed.

Proposed Technique

To be successful, the monitoring technique needs not only to obtain a representative sample, but also to be cost effective and possess a reasonable degree of simplicity. Two approaches could be used to achieve these goals:

- Sample port hardware could be further researched and a consensus of a simple, cost-effective, reliable, sample port-probe device be mandated by regulation, or

- Hardware choice could be left to the choice of operator, and a set of QA/QC criteria be made a part of regulation.

Once samples are accessed, a condensing coil should be used to quickly cool the sample to ambient conditions. A design set-up similar to the Porcupine probe referenced on page B-31 of the Battelle PNL manual--
Sampling and Analysis Methods for Geothermal Fluids and Gases would closely approximate the typical liquid sampling arrangement envisioned.

Documentation of sampling conditions will be essential to interpretation and defense of a sample taken in the production mode of waste fluid injection. A suggested list of data to be obtained includes:

- o T&P of flowline at sampling point
- o Conductivity of flowline at sampling point
- o T&P of sample line
- o Conductivity & T of sample
- o Barometric pressure
- o Vortex metering of fluid volumes disposed
- o List of production wells of flowrates on line to disposal well
- o T, P, % steam drawn from individual separators on line

Most of these data will routinely be recorded by operators and should be available.

It is implicit in the neglect to specify sample port locations that a liquid full flow line is assumed. Verification of this fact will be necessary at each sample site to ensure that two-phase sampling techniques are not required. Other than this requirement, sample port location should be near the injection well so as to adequately characterize the fluid subsequent to any surface scaling or corrosion that may alter the fluid chemistry.

Conclusions and Recommendations for Further Research

- o Define a standard or alternative standard method for design or verification of adequacy of design for sampling ports.
- o Establish a reporting system that will allow an estimate of total flow through of potentially hazardous material as a function of time.
- o For those species which may have significant partitioning tendencies between steam-water phases, establish a threshold temperature limit above which sampling for these species may require that special precautions be taken. Do any such species exist in disposal brines particularly in those geothermal process systems that have undergone a steam flash separation?
- o Establish frequency of sampling guidelines on the basis of either changes in continuous monitoring records (conductivity) or on the basis of analytic reproducibility within a set limit of variation.

In summary, although some site specific problems may be encountered in monitoring the disposal of liquid geothermal wastes, existing technology

should allow representative sampling of the effluent. Establishment of guidelines for monitoring should address the high temperature sampling problem through evaluation of this existing technology. Reporting criteria may need to be upgraded to allow establishment of control strategies, but species of concern will be site specific both as to content in the resource base and as to their content in the planned zone of disposal. Thus control strategies are likely to be site specific in nature.

Water Sampling Requirements for Cold Water Injection Systems

Introduction

In general, cold water injection refers to the injection of water from a storage pond into an injection well. In geothermal applications, this would mean that the resource conversion unit would dump spent geothermal water into a storage pond for cooling and possible chemical treatment before injection.

The advantages of this type of system are:

- The spent geothermal water can be chemically treated to remove problem chemical elements.
- High silica concentrations can be reduced by precipitation before injection.
- Elimination of high temperature components simplifies much of the injection system.

The disadvantages of this type of system are:

- The increased quantity of solid wastes.
- The increase in filtering capacity.

Purpose of Water Sampling

Water sampling for regulatory purposes needs to accomplish the following:

Resource Conversion Effluents

- To determine the quantity of toxic and noxious elements that can become airborne when the spent geothermal water is released to the pond.
- To determine the chemical composition of the spent geothermal water so the chemical composition of the pond sediments can be determined.
- To determine the chemical composition of the fluid so chemical treatment for specific chemical elements may be initiated and maintained.

Injection Effluents

- To determine and monitor the quantity of chemical elements being injected so compliance with regulatory agencies can be maintained.
- To monitor elements that corrode components of the injection system.
- To monitor the total dissolved and suspended solids being injected.

Storage Pond Effluent

- To determine and monitor the chemical composition of the pond water to be aware of and possibly prevent chemical hazards from developing.
- To determine if chemical elements exist that may damage the storage pond liner.
- To monitor the pond water so the chemistry of the pond sediments can be determined.

Sampling Techniques

Resource Conversion Effluents

Sample taps should be placed in the line carrying the spent geothermal water to the storage pond. As the water temperatures can be as high as 125°C, samples should be collected through a condenser to eliminate possible steam loss and hazard to the person collecting the sample. The sample should be collected in a plastic bottle and the preservation techniques described in the section on preservation techniques in this report be initiated immediately. Samples should be collected and analyzed at least weekly. Increased sample frequency should be considered in applications where large effluent discharges exist.

Injection Effluent

Sample taps should be placed in the injection line between the filters and the well head. Generally the injection water is cool enough that sample collection through a condenser is not necessary. Samples should be collected in a plastic bottle and preserved immediately. Sampling frequency at this location should be at least every 24 hours.

Storage Pond Effluents

Samples of the storage pond water should be collected using dip sample techniques. Samples should be collected below the pond surface and at locations such that a composite sample can be prepared that is representative of the pond water. The samples should be collected in plastic bottles and preserved immediately.

Samples should be collected at least monthly but should be collected at a frequency determined by the rate of change of the pond water.

Sampling techniques of filtered materials, sediments and sludges are described in the section on solid wastes in this report.

Reporting Criteria for Samples

Sample collection, sampling point location, temperature, pressure, date, time, number of samples taken, and any other information necessary to define the original sample environment should be documented for each sample so others may use the data obtained from these samples and correlate them to other situations.

Conclusion

The purpose of this section is to describe water sampling techniques necessary to obtain samples representative of the effluents at the release points of the geothermal resource conversion system. This section outlines briefly a water sampling methodology that blends simplicity and adequacy. Sampling methods development is needed in the following areas:

1) gas-liquid sampling.

2) impact of air on geothermal water samples.

3) in-line monitoring.

CONCLUSIONS

The U.S. Environmental Protection Agency should consider alterations or additions to its policies in the geothermal sampling and analytical methods areas to:

- o better relate the degree of hazard represented by the control criteria levels to the need for accuracy in the measurement loadings, and, in turn better relate that need to the requirement for accuracy and precision in sampling and analysis;
- o provide for the use of alternative sampling methods and sampling sites within a geothermal operational system that will, from a technical standpoint, allow more accurate emission determinations than those that result from sampling at the point(s) of emission;
- o allow for a continuing and flexible system of sampling methods, research and development, that recognizes the wide differences in the character of geothermal sites;
- o provide for a continuing repository of sampling and analytical methods information available to the industry and regulators; and,
- o facilitate the cooperative development of sampling methods by all interested parties in the geothermal community.

The matrix cell (Figure 1) represents an integrated program toward geothermal effluent sampling. Each particular matrix cell represents the integration of three factors:

- o particular site
- o components of concern
- o release points

The integrator that binds these three factors together is the sampling method.

In order to integrate these factors to provide effluent monitoring to meet the effluent precision and accuracy goals, it may be that more than one sampling method will be necessary due to site-specific concerns of chemistry or specific utilization technologies.

The tying together of these factors will permit the identification of those methods most in need of additional work. These methods will be

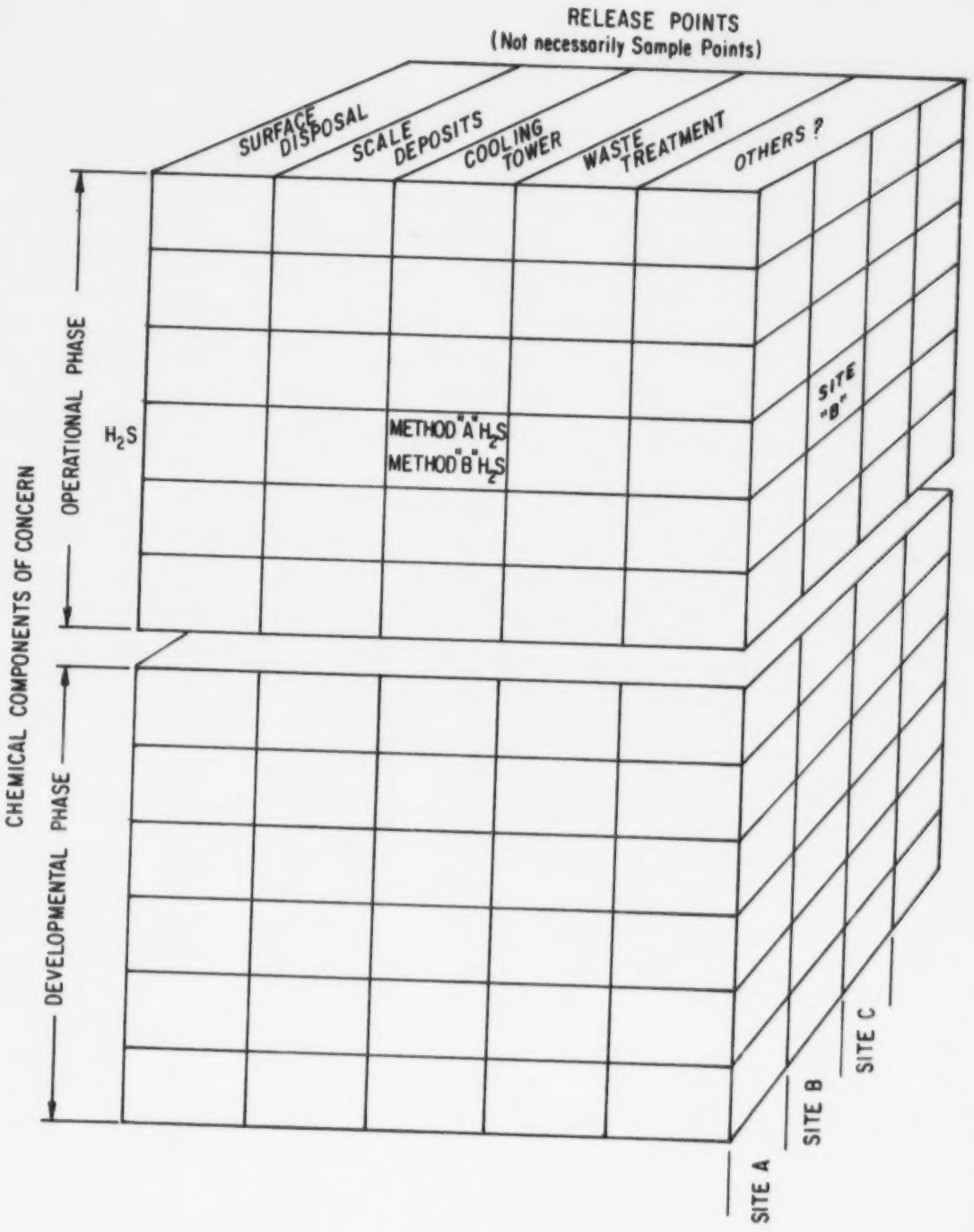

Figure 1. Proposed Matrix of Sampling Methods (for release leading to standardization of sampling documentation and sampling methods).

identified by:

- o risk of the component of concern
- o difference between the needed and currently available precision and accuracy performance
- o number of sites affected

In light of these factors, EPA can achieve a technical basis for measuring geothermal effluents through a directed and trackable program.

It is recognized that components of concern (pollutants and possibly nonpollutants) issue from various release points, i.e., surface disposal, cooling towers, etc., but that sampling methods applicable to these components and release points will vary from resource to resource and perhaps from application to application within a resource. In other words, components of concern are very often site specific because of resource chemistry, plant design, etc.

We are suggesting a three-dimensional matrix that will identify as a cell within the matrix applicable sampling methods for a component at a release point of a geothermal site. By identifying those methods that are applicable in the three dimensions, we are left with open cells in the matrix that identify components, release points, and sites for which there are not available applicable methods and for which the sampling methods must be developed.

It is further suggested that the matrix be duplicated for operational and developmental sites.

The objectives of the duplication are that early in the development EPA become involved in the development to the extent that it become familiar with the expected problems of sampling at that site. The EPA could/should work with the developer in ascertaining which, if any, existing sampling methods are applicable and support development work for those for which an applicable method is not available.

As development progresses to operational status, the methods will be elevated to the appropriate cell in the operational matrix.

The matrix helps priority rank the problem areas which need work and if "interferences" are included in the cells, it will identify these methods which can or cannot be used at other sites.

The selection of methods will be by mutual (hopefully) agreement between developer and EPA and if required, outside agencies and/or the developers of the methods. The big advantage is that site developer and EPA both being familiar with the site specific problem can work together. EPA's incentive to participate follows from its regulatory role, of course. The developers incentive may well lie in shortening the permitting process.

The procedures for sampling and analysis are composed of many steps, with a characteristic imprecision inherent in each. Some steps are more difficult to do precisely than others. The imprecisions of all the steps in the procedure yield the characteristic uncertainty of an analytical result. A thorough and accurate appraisal for the components of variance yields two practical results. One is the identification of which steps or portions of procedures contribute the most to overall uncertainty. This provides stimulation for finding alternative steps or procedures that are more stably done in the sense of comparing or seeking alternative sampling/analysis methods or in making improvements to a basic approach.

Secondly, this kind of review will show what is possible, in the sense of anticipated degree of comparability among methods and of the limits in precision that can be expected for even a well-done sampling/ analysis method.

The study/research recommended here is to first identify, on paper, all the steps techniques and factors which are present in a sampling/ analysis method; secondly to assign well-considered numerical values to the factors et al. in order to calculate separated values for the variances; and thirdly to combine them into an expected standard deviation. As a check on the procedure above, the real counterparts of the sampling/analysis methods should be performed so that empirical values may be deferred for some individual and some grouped components of variance.

Such a study is appropriate for each component of concern (potential pollutant) and each sampling/analytical method. As a practical matter, initial screening of proposed sampling/analytical methods would likely identify several items of commonality, results for which could be applied generally. Also, certain inferior or inherently imprecise (sensitive) steps to insight could be identified early, perhaps leading to a rejection of the method without further study.

This approach will provide a quantitative and defendable (reviewable) method for deciding whether alternative methods are indeed comparable. Additionally, it would yield guidelines for deciding whether (when) improvements to existing methods would be no longer cost-effective to pursue.

This same kind of evaluation about components of variance applies to the models which describe the pathways and processes in the environment or in operating geothermal plants. The accuracy and uncertainty in the calculated conditions in the compartments of the models depend jointly on the data used to feed the model and on the uncertainty of transfer coefficients et al. that are part of the model.

When these models are used, their reliability (uncertainty) should be given. The numerical value for that reliability can be obtained from a review procedure analogous to the one described for determining overall variance for a sampling/analysis method. In practice, analytical data fed to the model carry their own uncertainty value which should be considered in order that the final calculated result can be assigned a reliability factor.

It is important that a forecast or qualification of the effluents involve a linking of the plant characteristics with the available data, not only in control values of concentration, but also in regard to the uncertainties involved.

The objective of the research needs identified in this workshop is the development of geothermal effluent sampling techniques which:

- o accurately monitor effluent discharge
- o are accurate, precise and repeatable within specified limits
- o are readily and inexpensively implemented.

In some instances, these criteria may be most effectively realized by sampling the geothermal material at other than the precise discharge or release point.

The example presented is the identified problem of sampling cooling tower discharge. Sampling at the top of the tower is problematic due to the dimensions of the discharge opening, turbulence, and the nonhomogenous nature of the discharge. On the other hand, determination of the effluent discharges might be more readily accomplished by sampling the flux of material through the other portions of the system and calculating the discharge by difference.

In one hypothetical system, for example, we might find that H_2S partitions strongly into the cooling tower discharge. Sampling and measurement of H_2S at the cooling tower inflow would yield a maximum estimate of the flux of H_2S discharged to the environment from the tower. In many cases, this would be entirely sufficient to ensure compliance and is likely to be more readily accomplished, perhaps with better accuracy and precision.

We recommend research directed toward testing the specific cooling tower sampling procedure presented here and in general toward testing the concept of sampling discharges at points other than at the precise plant/ environment boundary. Evaluation should include an assessment of physical practicality and simplicity as well as an assessment of variance described in our first recommendation.

SUMMARY OF RECOMMENDATIONS

Gas-

- Continuous in-line monitoring
- Cooling tower emissions
- Pipeline sampling
- Mercury sampling/fixing
- Matrix gases
- H_2S field analysis
- Non-volatile sampling
- Sample degradation

Two-Phase-

- Sampling strategies
- Accuracy
- Reproducibility
- Preservation
- Effects of Solids
- Sampling hardware
- Fluid mechanics
- Chemical concerns
- Policy guidelines
- Appropriate techniques
- Multiphase flow description
- Hardware evaluation
- Application of technique to environment

Liquid-

- Definitions
- Procedures
- Evaluation
- Special techniques
- Sample collection/treatment
- Process by-products/holding pond tailings
- Direct release into surface waters
- Effect of dissolved oxygen
- Closed loop injection
- Cold water injection